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PHYSICAL CHEMISTRY OF SOLUTIONS

The Solubility of Fullerene C_{60}–Fullerene C_{70} Mixtures in Styrene at 25°C

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Abstract—The solubility of fullerene C_{60}–fullerene C_{70} mixtures in styrene was studied under isothermal conditions at 25°C. The corresponding solubility isotherm is given and characterized.

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INTRODUCTION

Studies of the solubility of fullerenes are of importance for the development of methods for chromatographic and prechromatographic (based on solubility and extraction equilibria) separation of industrial fullerene mixtures and for studies of chemical reactions with the participation of fullerenes [1–7]. There are ample experimental data on the solubility of pure light (C_{60} and C_{70}) fullerenes in various inorganic and diverse organic solvents (alkanes, aromatic solvents, alcohol, carboxylic acids, ionic liquids, etc.). The solubility of C_{60} was studied in more than 170 solvents, and that of C_{70}, in more than 30 solvents [8].

Note that the special feature of the corresponding works is the presence of data predominantly on binary systems, such as light fullerene–solvent systems. There is almost no data on the solubility of a pure fullerene in mixed solvents or of a mixture of fullerenes in one solvent [4–6, 9], in spite of their great importance for the optimization of separation conditions. The number of works concerned with solubility in ternary systems of the fullerene C_{60}–fullerene C_{70}–solvent type is also exceedingly limited. Exceptions are works [10, 11], in which solubility in the C_{60}–C_{70}–1,2-dimethylbenzene system was studied at various temperatures.

In [10], solubility in this system was studied at –20, 25, and 80°C; it was found that two $(C_{60})_x(C_{70})_{1-x} \cdot n(o\text{-}C_6H_4(CH_3)_2)$ substitution solid solutions always crystallized. At 80°C, both solid solutions were unsolvated, at 25°C, the solid solution enriched in C_{60} was bisolvated and the solution enriched in C_{70}, unsolvated, and at –20°C, both solid solutions were bisolvated. It was also shown that there was a eutonic point corresponding to a discontinuity in the crystallization of solid solutions. Conversely, the authors of [11] observed three solid phases and two eutonic points in the C_{60}–C_{70}–1,2-dimethylbenzene system with the formation of two three-phase fields in the phase diagram. At 298 K, solid solution was based on $C_{60} \cdot 2(o\text{-}C_6H_4(CH_3)_2)$–eutonic(1)–constant-composition phase $(C_{60})_{0.22}(C_{70})_{0.78} \cdot 4(o\text{-}C_6H_4(CH_3)_2)$ and $(C_{60})_{0.22}(C_{70})_{0.78} \cdot 4(o\text{-}C_6H_4(CH_3)_2)$–eutonic(2)–$C_{70} \cdot 2(o\text{-}C_6H_4(CH_3)_2)$; at 330 K, C_{60}–eutonic(1)–constant-composition phase $(C_{60})_{0.22}(C_{70})_{0.78} \cdot 4(o\text{-}C_6H_4(CH_3)_2)$ and $(C_{60})_{0.22}(C_{70})_{0.78} \cdot 4(o\text{-}C_6H_4(CH_3)_2)$–eutonic(2)–$C_{70} \cdot 2(o\text{-}C_6H_4(CH_3)_2)$; at 360 K, C_{60}–eutonic(1)–constant-composition phase $(C_{60})_{0.22}(C_{70})_{0.78} \cdot n(o\text{-}C_6H_4(CH_3)_2)$, where $n < 4$, and $(C_{60})_{0.22}(C_{70})_{0.78} \cdot n(o\text{-}C_6H_4(CH_3)_2)$–eutonic(2)–$C_{70} \cdot 2(o\text{-}C_6H_4(CH_3)_2)$; and, at 380 K, C_{60}–eutonic(1)–constant-composition phase $(C_{60})_{0.22}(C_{70})_{0.78} \cdot n(o\text{-}C_6H_4(CH_3)_2)$, where $n < 4$, and $(C_{60})_{0.22}(C_{70})_{0.78} \cdot n(o\text{-}C_6H_4(CH_3)_2)$–eutonic(2)–$C_{70}$.

Note that the importance of studying the solubility of fullerenes in styrene is largely determined by the possibility of the optimization of thermocatalytic styrene polymerization conditions for the production of polystyrene modified with fullerenes with unique service characteristics [12, 13].

EXPERIMENTAL

We used pure fullerenes C_{60} and C_{70} (99.5%) with the main detectable impurities C_{60} in C_{70} and C_{70} in C_{60} (~0.5 wt %) and a fullerene mixture 39% C_{70}, 60% C_{60}, 1% C_n ($n > 70$) from ZAO ILIP (St. Petersburg), *o*-xylene of ch. d. a. (pure for analysis) grade, toluene of ch. d. a. grade, and styrene of ch. d. a. grade. The purity of the reagents was controlled chromatographically and by measuring refractive indices and boiling temperatures.

The isothermal solubility in the C_{60}–C_{70}–styrene system at 25°C was studied by the isothermal saturation method. First, homogeneous mixtures (solid solutions) of fullerenes of various compositions were prepared by dissolving certain amounts of pure fullerenes and fullerene mixture in toluene followed by evaporation at 40°C in air. Toluene was selected for the prepa-

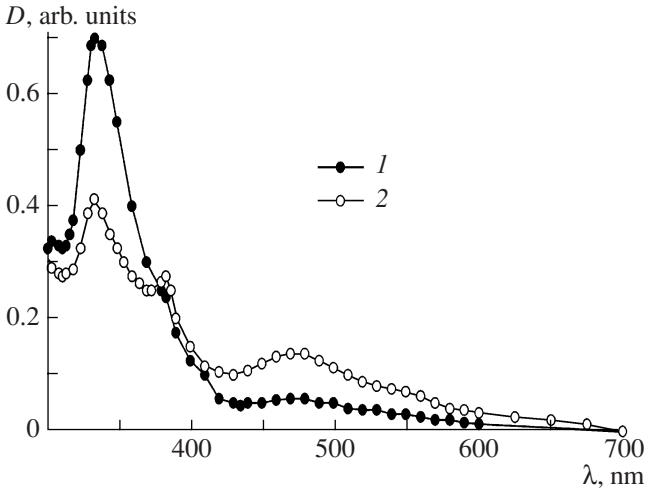

Fig. 1. Optical spectra of solutions saturated with respect to solid solutions (*1*) $(C_{60})_{0.75}(C_{70})_{0.25}$ and (*2*) $(C_{60})_{0.20}(C_{70})_{0.80}$ (weight fractions). Dilution with xylene 1 : 900, styrene in *o*-xylene (the same dilution) as a reference solution.

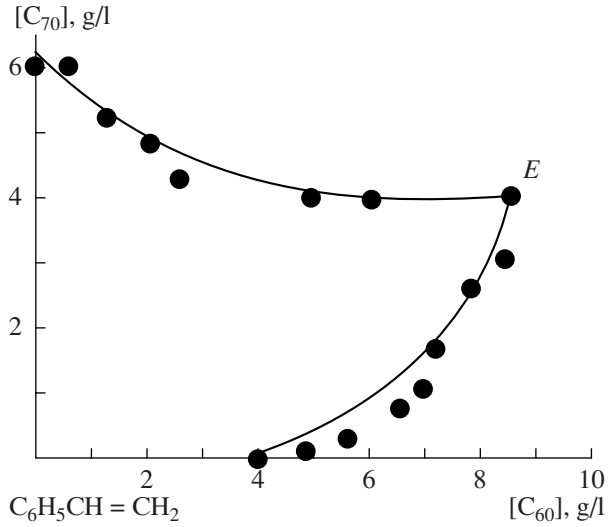

Fig. 2. Solubility diagram for the C_{60}–C_{70}–styrene system at 25°C.

ration of solid solutions because of a fairly high solubility of fullerenes in it and a fairly low (compared with the other aromatic solvents) enthalpy of vaporization. At the next stage, styrene was saturated with solid solutions (fullerenes were always taken in a large excess, 50 mg of fullerenes per 4 ml of styrene) at 25 ± 0.1°C in a temperature-controlled shaker for 20–30 h. The attainment of stationary solubility values was checked by taking samples in certain time intervals and determining their concentrations.

For analyses, solutions were separated from the solid phase by filtration on a Schott filter (porosity 10). Concentrations after saturation with solid solutions were determined spectrophotometrically on a Specord M-32 spectrophotometer at λ = 335.5 and 472.0 nm. For analyses, aliquots of solutions of C_{60}, C_{70}, or fullerene mixture in styrene were taken and diluted with *o*-xylene. A solution of styrene in *o*-xylene of the same dilution as the samples analyzed was used as a reference.

The concentrations of C_{60} and C_{70} in saturated solutions were calculated using empirical dependences obtained for solutions in *o*-xylene [13],

$$c_1 = 13.10(D_{335} - 1.808D_{472}), \quad (1)$$

$$c_2 = 42.51(D_{472} - 0.0081D_{335}), \quad (2)$$

where D_{335} and D_{472} are the optical densities of solutions related to the absorbing layer thickness 1 cm and c_1 and c_2 are the concentrations of C_{60} and C_{70}, respectively (mg/l). We ignored insignificant amounts of so-called higher fullerenes. The data on the contents of fullerene components in the solid phase (solid solution) were also obtained spectrophotometrically after dissolving the solid in *o*-xylene (with *o*-xylene as a reference solution).

RESULTS AND DISCUSSION

The electronic absorption spectra of solutions in styrene saturated with respect to the $(C_{60})_{0.75}(C_{70})_{0.25}$ and $(C_{60})_{0.20}(C_{70})_{0.80}$ solid solutions are shown by way of example in Fig. 1. Note that the spectra do not exhibit solvatochromic effects and are fully analogous to the corresponding spectra in aromatic solvents (*o*-xylene, benzene, toluene, and *o*-dichlorobenzene). The use of empirical equations (1) and (2) is therefore justified. Such a stability of the absorption spectra of fullerenes at λ = 335 nm with respect to solvent changes is only observed in the region of dilute solutions; at λ = 472 nm, much more concentrated solutions can be used.

The experimental data on the composition of the equilibrium liquid phase of the C_{60}–C_{70}–styrene ternary system at 25°C are shown in Fig. 2. We see that the salting in effect is observed in the system on the branch of the crystallization of solid solutions enriched in C_{60}; that is, the solubility of C_{60} increases as the concentration of C_{70} grows. Conversely, the salting out effect is observed for the branch of the crystallization of solid solutions enriched in C_{70}, and the solubility of C_{70} decreases as the concentration of C_{60} grows. Note that similar phase effects were observed in [10] in the C_{60}–C_{70}–1,2-dimethylbenzene system at –20, 25, and 80°C.

The experimental data on the compositions of the equilibrium liquid and solid phases in the C_{60}–C_{70}–styrene system at 25°C are listed in the table. Figure 3 presents a diagram of the distribution of fullerene components between the liquid and solid phases. According to our data, along the crystallization branch of solid solutions enriched in C_{60} (c_1 = 4.02–8.46 g/l), bisolvated solid substitution solutions $(C_{60})_x(C_{70})_{1-x}$ ·

Compositions of equilibrium liquid and solid phases in the C_{60}–C_{70}–styrene system

c_1	c_2	y	x	Solid phase
4.02	0.00	1.00	1.00	$(C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2$
4.88	0.11	0.98	0.93	$(C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2$
5.64	0.32	0.95	0.89	$(C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2$
6.55	0.77	0.90	0.83	$(C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2$
6.96	1.08	0.87	0.80	$(C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2$
7.20	1.70	0.80	0.75	$(C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2$
7.84	2.63	0.75	0.70	$(C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2$
8.46	3.08	0.73	0.67	$(C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2$
8.55	4.00	0.64	0.59	$(C_{60})_x(C_{70})_{1-x} + (C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2$
6.03	3.99	0.60	0.50	$(C_{60})_x(C_{70})_{1-x}$
4.97	4.02	0.55	0.40	$(C_{60})_x(C_{70})_{1-x}$
2.61	4.30	0.39	0.30	$(C_{60})_x(C_{70})_{1-x}$
2.07	4.85	0.30	0.20	$(C_{60})_x(C_{70})_{1-x}$
1.27	5.25	0.19	0.15	$(C_{60})_x(C_{70})_{1-x}$
0.60	6.02	0.09	0.05	$(C_{60})_x(C_{70})_{1-x}$
0.00	6.02	0.00	0.00	$(C_{60})_x(C_{70})_{1-x}$

Note: c_1 and c_2 are the concentrations of C_{60} and C_{70} in solution, g/l; y is the fraction of C_{60} in liquid solution, wt %; and x is the fraction of C_{60} in solid solution.

$2C_6H_5CH{=}CH_2$ containing two styrene molecules crystallize. Conversely, along the crystallization branch of solid solutions enriched in C_{70} (c_2 = 3.99–6.02 g/l), nonsolvated solid substitution solutions $(C_{60})_x(C_{70})_{1-x}$ that do not contain styrene crystallize. At c_1 = 8.55 g/l, the solid phase has the composition $(C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2 + (C_{60})_x(C_{70})_{1-x}$. Note that two types of solid solutions also crystallize in the C_{60}–C_{70}–1,2-dimethylbenzene system at 25°C [10]; bisolvated solid solution crystallizes along the branch of crystallization of solid solutions enriched in C_{60}, and nonsolvated solid solution, along the branch of crystallization of solid solutions enriched in C_{70}.

Information about the content of solvent molecules in solid solutions was obtained from the data on polythermal solubility of pure light fullerenes (C_{60} and C_{70}) in styrene. The polytherm of solubility of C_{60} has a dome shape, which is evidence that solution is accompanied by solvate formation (the $C_{60} \cdot 2C_6H_5CH{=}CH_2$ bisolvate). It follows that the solid phase at equilibrium with saturated solution in the C_{60}–styrene binary system is bisolvated C_{60} up to 40°C; at 40°C, the crystal solvate dissolves incongruently to produce unsolvated C_{60}. At higher temperatures, the solid phase at equilibrium with saturated solution is unsolvated C_{60}. Conversely, the solubility polytherm of C_{70} in styrene has a sigmoid shape, which is evidence that no solvate formation occurs in solution.

Note that a discontinuity is observed in the C_{60}–C_{70}–styrene system at 25°C. This discontinuity corresponds to the conjugation angle in the crystallization of solid solutions, the immiscibility region corresponds to $0.5 < x < 0.6$ (Fig. 3). The system also contains a nonvariant (at a constant pressure) eutonic point E [14] (Fig. 2) corresponding to joint saturation with two solid solutions $(C_{60})_{0.6}(C_{70})_{0.4} \cdot 2C_6H_5CH{=}CH_2$ and $(C_{60})_{0.5}(C_{70})_{0.5}$. The isothermal solubility diagram of the

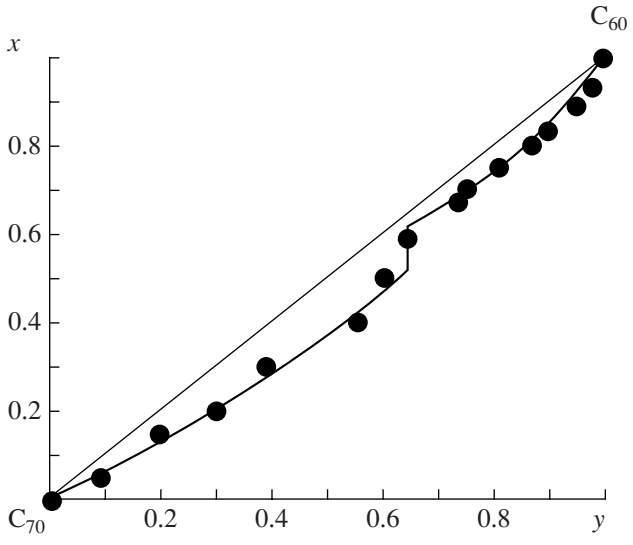

Fig. 3. Distribution of fullerene components between the liquid and solid phases in the C_{60}–C_{70}–styrene system at 25°C; x and y are the weight fractions of C_{60} in C_{60} + C_{70} mixtures in the liquid and solid phases in the solvateless concentration space.

ternary system at 25°C has the same structure as the solubility diagram of the C_{60}–C_{70}–*o*-xylene system [10].

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